CHAPTER IV

RESULTS

4.1 Quantity of Silver from Various Fixing Solution Waste

The results of the experiment with the aid of atomic absorption spectrophotometer (A.A.S.) for standard silver solution and various sources of used fixing solution are presented in Table 4.1 and Table 4.2 respectively. The standard silver solution were also presented graphically in Fig. A1 in Appendix I.

Instrument conditions used

Wavelength	328.1	nm.
Lamp width	3.0	mA.
Slit width	100	μ
Slit height	10	mm.
Air pressure	15	psig
Air : Aceteline	3 : 7	

Table 4.1 Absorbance of standard silver solution from A.A.S.

Std. Silver Solution (p.p.m.)	Absorbance			Average absorbance
	I	II	III	
1	4	4	4	4.00
2	9	8	9	8.66
4	18	19	18.5	18.50

Table 4.1 Absorbance of standard silver solution from A.A.S.

(continue)

Std. Silver Solution (p.p.m.)	Absorbance			Average absorbance
	I	II	III	
6	30	28	28	28.66
8	35	36	36	35.66
10	48	47	47	47.33

Table 4.2 Silver concentration of various fixing solution waste.

Source of used fixing solution	Type of + film	pH of fixing	Volume # litre/Day	Average * Absorbance	Ag g/litre	Quantity of Silver g/Day
Rochester color lab	P.F.	5.91	60	29.33	6.3	378.0
Technic color lab	P.F.	6.40	66	26.00	5.6	369.6
Kodak Thailand Co.Ltd.	P.F.	6.65	45	34.00	7.3	328.5
Saha color lab	P.F.	5.26	48	27.50	5.9	283.2
Vity cene color lab	M.F.	5.72	55	23.66	5.1	280.0
Cenae color lab	M.F.	5.01	60	18.50	4.0	240.0
Directorate of photo-graphy, RTAF.	A.F.	5.50	32	35.0	7.5	240.0
First color lab	P.F.	5.86	35	31.17	6.7	234.5
C.P.S. color lab	P.F.	4.72	53	20.66	4.4	233.2
Rama hospital	X.F.	6.44	25	42.83	9.2	230.0
Directorate of mapping RTAM.	A.F.	5.25	27	38.17	8.2	221.0

Table 4.2 Silver concentration of various fixing solution waste. (continue)

Source of used fixing solution	Type of + film	pH of fixing	Volume # (litre/Day)	Average * Absorbance	(Ag) g /litre	Quantity of Silver g /Day
Phumipol hospital	X.F.	5.56	23	41.83	9.0	207.0
Thai color lab	P.F.	5.89	30	28.0	6.0	180.0
Phramongkut hospital	X.F.	6.03	20	34.5	7.4	148.0
Agfa photo finishing center	P.F.	6.36	20	34.5	7.4	148.0
Siriraj hospital	X.F.	6.16	20	30.17	6.5	130.0
Rhognsilp cenae lab	M.F.	5.82	30	20.00	4.3	129.0
Paolo memorial hospital	X.F.	4.96	8	51.17	11.0	88.0
Computer color lab	P.F.	4.93	16	23.66	5.1	81.6
Pathumvan X-ray lab	X.F.	5.56	5	52.00	11.2	56.0
Pure color lab	P.F.	6.18	10	25.17	5.4	54.0
Samsaen X-ray	X.F.	5.39	5	47.00	10.1	50.5
Amorn color lab	P.F.	6.59	10	22.0	4.7	47.0
Paholyotin X-ray Co.Ltd.	X.F.	6.07	5	38.66	8.3	41.5

Table 4.2 Silver concentration of various fixing solution waste. (continue)

Source of used fixing solution	Type of+ film	pH of fixing	Volume # litre/Day	Average • Absorbance	Ag g/litre	Quantity of Silver g/Day
Phayathai X-ray Co.Ltd.	X.F.	5.11	5	33.00	7.1	35.5
Rother lab	P.F.	5.86	10	15.0	3.2	32.0
Wangburapa polyclinic	X.F.	6.57	3	34.5	7.4	22.2
Rama X-ray lab	X.F.	5.99	3	30.17	6.5	19.5

+ Type of film ; A.F. is aerial films, M.F. is motion picture films, P.F. is photofinishing films. and X.F. is X-ray films.

Volume per day are approximated volume which obtained by questionniare.

• In quantitative analysis by A.A.S., all these sample was diluted to ratio 1 : 1,000 before absorbance measurement.

4.2 Decomposition Potential of Pure Silver Complex ($NaAgS_2O_3$) Solution and Used Fixing Solution.

The results of the experiment on decomposition potential determination of pure silver complex ($NaAgS_2O_3$) solution and used fixing solution which have the same silver concentration 7.5 grams per litre are presented in Tables 4.3 and 4.4, and are also presented graphically in Figures 4.1 and 4.2 respectively. The decomposition potential were determined from these graph and shown in Table 4.5 including the current density observation at the time the first black particles were formed rapidly to become a serious dirt problem.

Table 4.3 Experimental data on decomposition potential determination of pure silver complex ($NaAgS_2O_3$) solution, Silver concentration : 7.5 g/l at temperature 30°c.

Applied Potential (volt)	Current (Amp.)		
	0 R.P.M.	500 R.P.M.	1,000 R.P.M.
0	0	0	0
0.2	0	0	0
0.4	0.02	0.04	0.05
0.6	0.12	0.15	0.20
0.8	0.14	0.32	0.40
1.0	0.22	0.48	0.75
1.2	0.28	0.75	1.05
1.4	0.32	1.10	1.35

Table 4.3 Experimental data on decomposition potential determination of pure silver complex ($NaAgS_2O_3$) solution, Silver concentration : 7.5 g/l at temperature 30°c. (continue)

Applied Potential (volt)	Current (Amp.)		
	0 R.P.M.	500 R.P.M.	1,000 R.P.M.
1.6	0.43	1.48	1.75
1.8	0.59	1.90	2.15
2.0	0.75	2.37	2.40
2.2	0.98	2.71	3.20
2.4	1.20	3.22	3.75
2.6	1.48	3.83	4.25
2.8	1.75	4.21	4.80
3.0	2.17	4.70	5.20
3.2	2.68	5.21	5.60
3.4	3.00	5.53	6.10
3.6	3.60	6.02	6.80
3.8	4.08	6.55	7.50
4.0	4.55	6.97	8.10

Table 4.4 Experimental data on decomposition potential determination of used fixing solution, Silver concentration : 7.5 g/l, at temperature 30°c.

Applied Potential (volt)	Current (Amp.)		
	0 R.P.M.	500 R.P.M.	1,000 R.P.M.
0	0	0	0
0.2	0	0	0
0.4	0.02	0.05	0.05
0.6	0.08	0.10	0.13
0.8	0.15	0.25	0.45
1.0	0.23	0.45	0.62
1.2	0.30	0.66	0.85
1.4	0.35	0.95	0.35
1.6	0.45	1.35	1.60
1.8	0.65	1.70	2.20
2.0	0.80	2.25	2.62
2.2	1.05	2.70	3.25
2.4	1.33	3.25	3.80
2.6	1.65	3.90	4.43
2.8	2.02	4.50	4.80
3.0	2.36	5.30	5.30
3.2	2.80	6.10	6.00
3.4	3.15	6.70	6.80
3.6	3.65	7.50	7.20

Table 4.4 Experimental data on decomposition potential determination of used fixing solution, Silver concentration : 7.5 g/l, at temperature 30°c

(continue)

Applied Potential (volt)	Current (Amp.)		
	0 R.P.M.	500 R.P.M.	1,000 R.P.M.
3.8	4.17	8.00	7.50
4.0	4.75	8.50	8.00

Table 4.5 Comparation of decomposition potentials at various speed of rotation and current observation at the time the first black particles were formed.

Rotation Speed (R.P.M.)	Pure silver complex		Used fixing solution	
	E_D (volt)	Current (Amp.)	E_D (volt)	Current (Amp.)
0	1.87	0.43	1.90	0.35
500	0.93	1.10	1.29	0.95
1,000	0.90	1.75	0.97	1.60

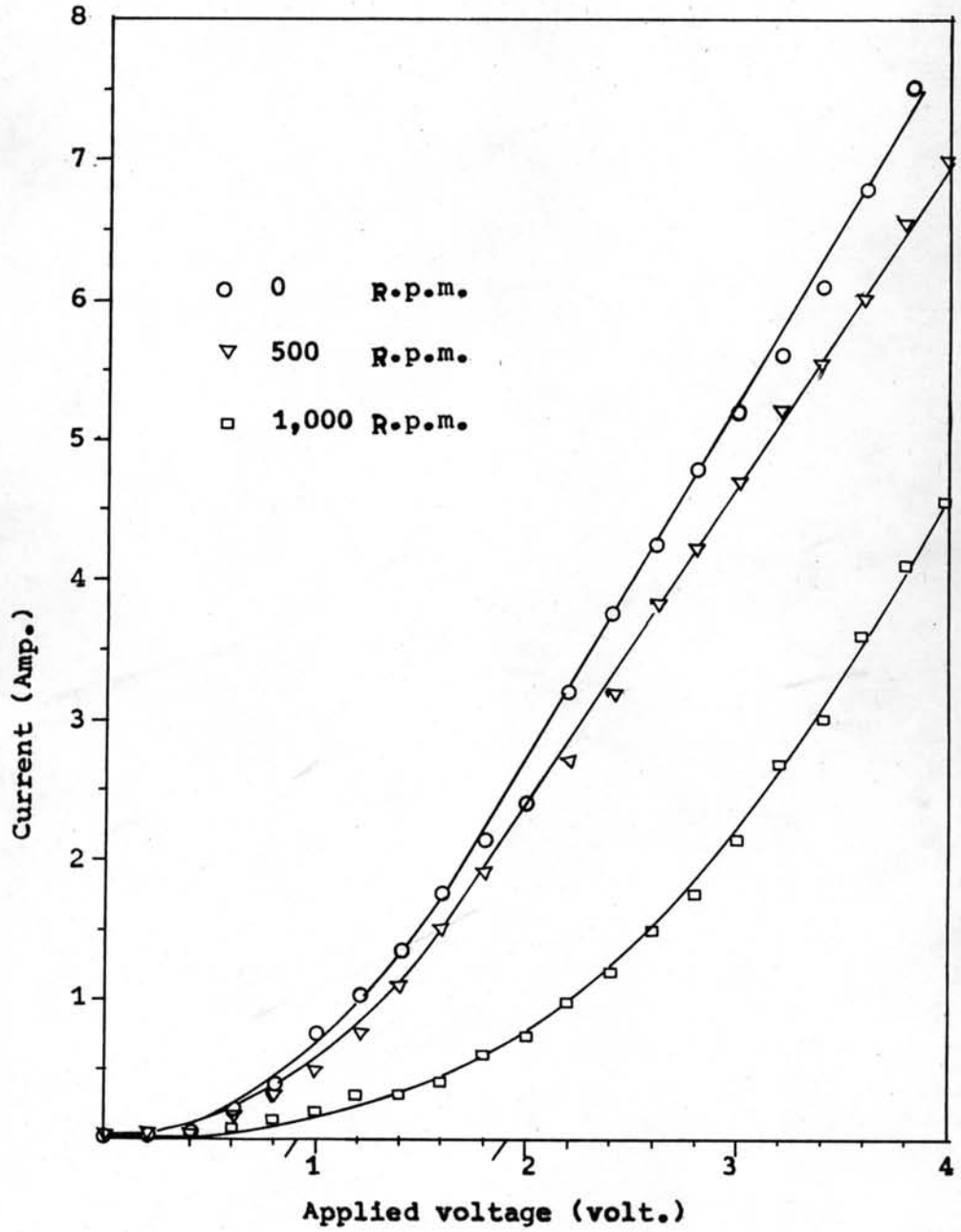

Figure - 4.1 Decomposition potential of pure silver complex Solution, Silver 7.5 g./l., at various cathode rotating speeds, Temperature 30°c E_D (0 r.p.m.) = 1.87 v., E_D (500 r.p.m.) = 0.93 v., E_D (1,000 r.p.m.) = 0.90 v.

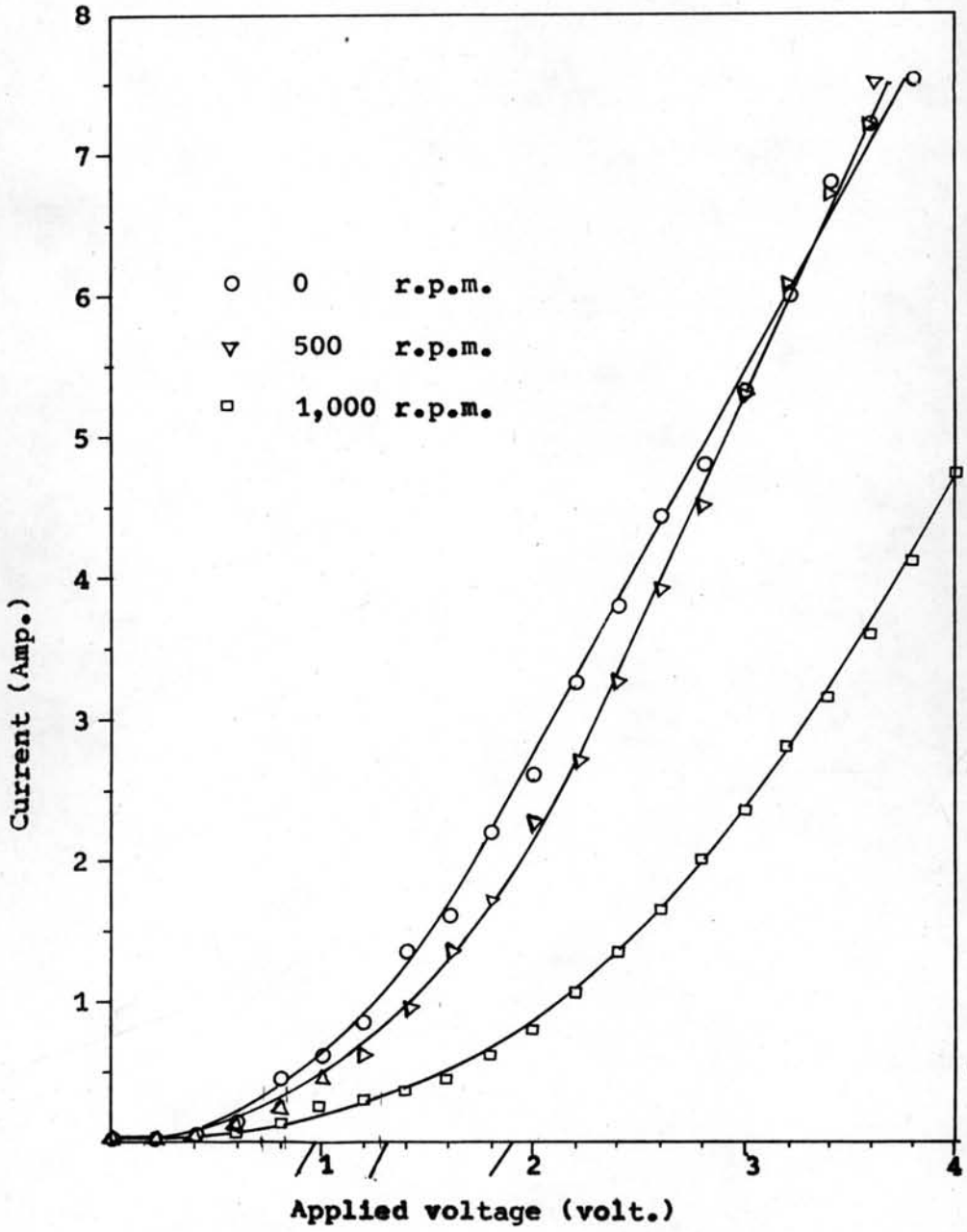

Figure 4.2 Decomposition potential of used fixing solution, Silver 7.5 g./l., at various cathode rotating speeds, Temperature 30°c, E_D (0 r.p.m.) = 1.90 v., E_D (500 r.p.m.) = 1.29 v., E_D (1,000 r.p.m.) = 0.97 v.,

4.3 Current Efficiency at Various Cathode Rotating Speed.

The results of the experiment on quantitative analysis of silver concentration in used fixing lolution during silver electrolytic cell operation by atomic absorption spectrophotometer at various time intervals are presented in Table 4.6 and are also presented graphically in Figure 4.3. The cathode rotating speed used were 200, 400, 600, 800 and 1,000 r.p.m. The results of calculation on current efficiency at the various cathode rotating speed are presented in Table 4.7 and are also presented graphically in Figure 4.4.

All experiments were operated at the following condition : E_{app} = 1.3 volt, current density = 0.3 asd., temperature = 30°c, initial silver concentration of used fixing solution = 7.5 g./l., and pH = 5.5.

Theoretical weight of deposited silver can be calculated by Equations 2.6 and 2.10

$$W = \frac{Wm\ (I \times t)}{96{,}493 \times n}$$

The experimental weight of deposited silver can be calculated from silver concentration data in Table 4.6 and the current efficiency can be calculated by using Equation 2.14

$$\eta = \frac{GM,\ expt.}{GM,\ theor.} \times 100$$

Table 4.6 Experimental results of silver concentration at various cathode rotating speed.

Time (min)	200 r.p.m.		400 r.p.m.		600 r.p.m.		800 r.p.m.		1,000 r.p.m.	
	av. absorbance	Ag g /l	av. absorbance	Ag g /l	av. absorbance	Ag g /l	av. absorbance	Ag g /l	av. absorbance	Ag g /l
0	34.83	7.50	34.83	7.50	35.00	7.50	35.00	7.50	34.83	7.50
30	30.00	6.45	30.00	6.45	29.50	6.35	29.33	6.30	29.50	6.35
60	25.66	5.50	24.50	5.25	24.50	5.25	24.00	5.15	23.33	5.00
90	20.33	4.35	20.17	4.33	19.17	4.10	18.66	4.00	17.83	3.85
120	15.66	3.35	15.00	3.20	13.50	2.80	12.83	2.75	14.66	3.15
150	11.17	2.40	10.50	2.25	8.17	1.75	7.50	1.60	8.17	1.75

Note : All. sample preparation for quantitative analysis by A.A.S were diluted with deionized water in dilution ratio 1 : 1,000

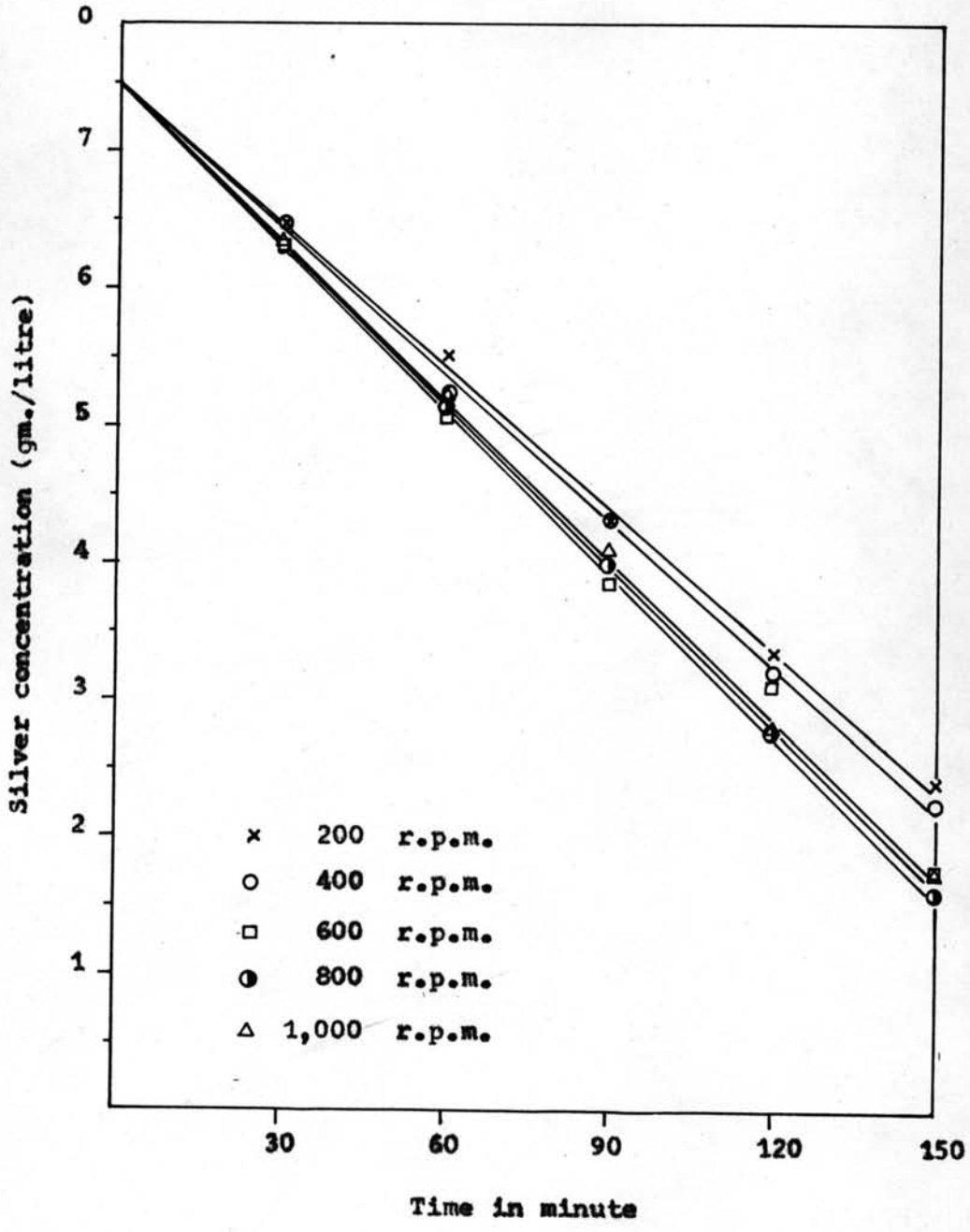

Figure 4.3 Silver concentration at various cathode rotating speeds, current density = 0.3 asd., pH = 5.50, Temperature 30°c, E_{app} = 1.30 volts.

Example at 200 r.p.m.

Theoretical deposited silver $= \frac{Wm\ (I \times t)}{96{,}493 \times n}$

$= \frac{107.88\ (.3 \times 150 \times 60)}{96{,}493 \times 1}$

$= 3.0186$ gm.

Experimental deposited silver $= (7.50 - 2.40) \times \frac{1}{2} - \frac{1}{1{,}000}$

$(6.45 + 5.50 + 4.35 + 3.35)$

$= 2.5500 - 0.0197$

$= 2.5303$ gm.

Current efficiency, η $= \frac{2.5303}{3.0186} \times 100$

$= 83.82$

Table 4.7 Current efficiency values of electrolytic silver recovery at various cathode rotating speed.

Rotating speed (r.p.m.)	Weight of deposited silver, g		Current efficiency
	Theoretical	experimental	
200	3.0186	2.5303	83.82
400	3.0186	2.6058	86.32
600	3.0186	2.8565	94.63
800	3.0186	2.9318	97.12
1,000	3.0186	2.8567	94.64

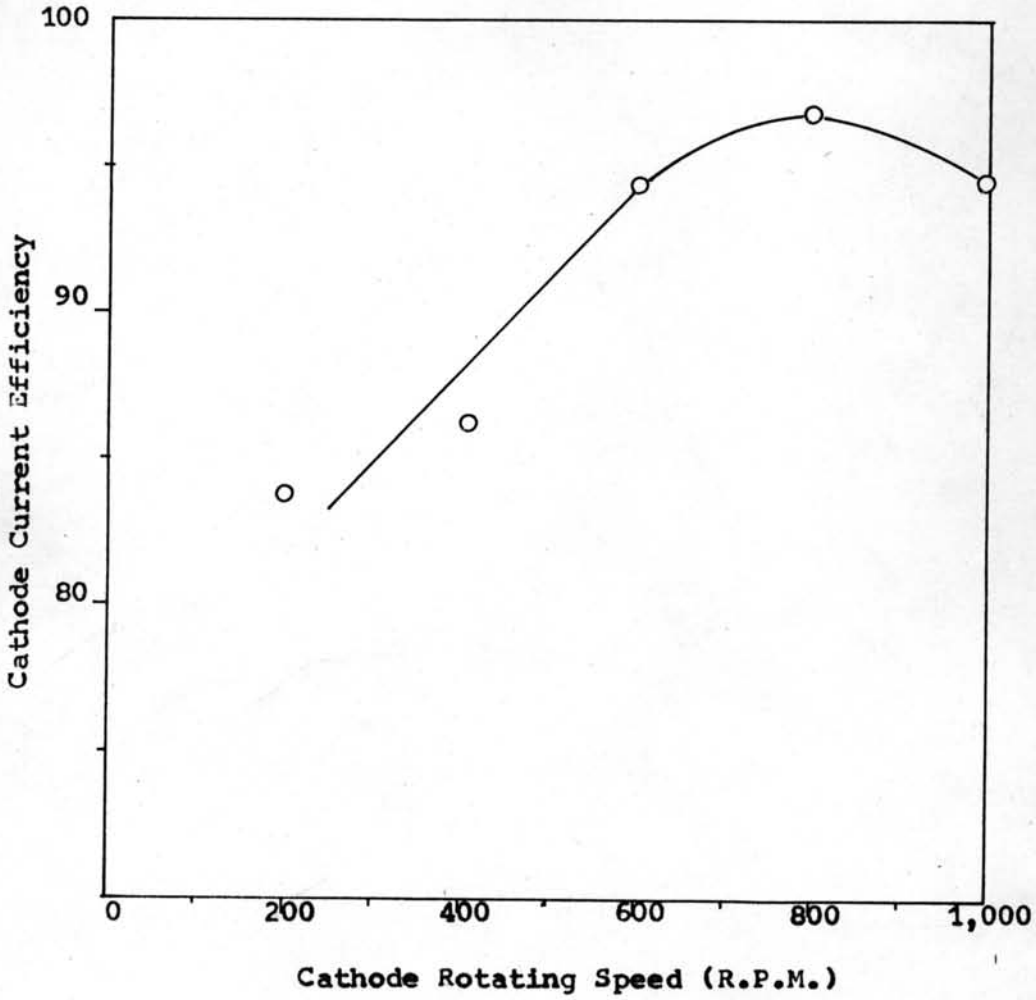

Figure 4.4 Dependence of cathode current efficiency on cathode rotating speed, current density = 0.3 asd., pH = 5.50, Temperature 30°c.

4.4 Current Efficiency at Various pH and Current Density

The results of the experiment on the current efficiency determination at various current density for various pH of used fixing solution are presented in Tables 4.8, 4.9, 4.10. 4.11, 4.12, 4.13 and 4.14 and are also presented graphically in Figure 4.5.

All experiment were operated at the following condition : E_{app} = 1.2 - 1.5 volts, rotating speed = 800 r.p.m., temperature = 30°c, initial silver concentration of used fixing solution = 7.5 g /l , and the quantity of glacial acetic acid and 12 N. sodium hydroxide used to control the pH were as presented in Table 4.15.

Table 4.8 Experimental results of current efficiency determination at various current density of used fixing solution pH = 3.8.

Current Density (asd.)	Yield (g)	0.1 N.KSCN ml.	Purity %	Wt. of Silver (g)		Current Efficiency
				Theor.	Expt.	
0.1	1.0361	9.03	97.41	1.3416	1.0093	75.23
0.3	1.2193	9.20	99.25	1.3416	1.2102	90.20
0.5	1.2340	9.17	98.92	1.3416	1.2207	90.99
0.7	1.2847	9.10	98.17	1.3414	1.2612	94.02
0.9	1.2584	9.00	97.09	1.3412	1.2218	91.09

Table 4.9 Experimental results of current efficiency determination at various current density of used fixing solution pH = 4.5

Current Density (asd.)	Yield (g)	0.1 N.KSCN ml.	Purity %	Wt. of Silver (g)		Current Efficiency
				Theor.	Expt.	
0.1	1.0656	9.13	98.49	1.3416	1.0495	78.33
0.3	1.2962	9.20	99.25	1.3416	1.2864	95.88
0.5	1.3082	9.07	97.84	1.3416	1.2799	95.40
0.7	1.3071	9.10	98.17	1.3414	1.2832	95.66
0.9	1.2366	9.15	98.71	1.3412	1.2206	91.10

Table 4.10 Experimental results of current efficiency determination at various current density of used fixing solution pH = 5.5

Current Density (asd.)	Yield (g)	0.1 N.KSCN ml.	Purity %	Wt. of silver (g)		Current Efficiency
				Theory	Expt.	
0.1	1.0823	9.20	99.25	1.3416	1.0742	80.07
0.3	1.3283	9.10	98.17	1.3416	1.3040	97.20
0.5	1.3287	9.10	98.17	1.3416	1.3044	97.23
0.7	1.2932	9.23	99.57	1.3414	1.2876	95.99
0.9	1.3026	9.07	97.85	1.3412	1.2746	95.03

Table 4.11 Experimental results of current efficiency determination at various current density of used fixing solution pH = 6.5

Current Density (asd.)	Yield (g)	0.1 N.KSCN ml.	Purity %	Wt. of Silver (g)		Current Efficiency
				Theor.	Expt.	
0.1	1.0981	9.13	98.49	1.3416	1.0815	80.61
0.3	1.3201	9.20	99.25	1.3416	1.3102	97.66
0.5	1.3403	9.17	98.92	1.3416	1.3258	98.82
0.7	1.3232	9.20	99.25	1.3414	1.3133	97.90
0.9	1.3191	8.97	96.77	1.3412	1.2765	95.17

Table 4.12 Experimental results of current efficiency determination at various current density of used fixing solution pH = 7.0

Current Density (asd.)	Yield (g)	0.1 N.KSCN ml.	Purity %	Wt. of Silver (g)		Current Efficiency
				Theor.	Expt.	
0.1	1.0693	9.20	99.25	1.3416	1.0613	79.11
0.3	1.3118	8.90	96.01	1.3416	1.2594	93.87
0.5	1.3279	9.17	98.92	1.3416	1.3136	97.90
0.7	1.3061	9.05	97.63	1.3414	1.2751	95.06
0.9	1.2808	9.13	98.49	1.3412	1.2614	94.05

Table 4.13 Experimental results of current efficiency determination at various current density of used fixing solution pH = 8.0

Current Density (asd.)	Yield (g)	0.1 N.KSCN ml.	Purity %	Wt. of Silver (g)		Current Efficiency
				Theor.	Expt.	
0.1	1.0402	9.10	98.17	1.3416	1.0212	76.12
0.3	1.2103	9.15	98.71	1.3416	1.1947	89.05
0.5	1.2973	9.07	97.84	1.3416	1.2693	96.62
0.7	1.2884	9.00	97.09	1.3414	1.2509	93.25
0.9	1.2485	9.15	98.71	1.3412	1.2324	91.89

Table 4.14 Experimental results of current efficiency determination at various current density of used fixing solution pH = 10.0

Current Density (asd.)	Yield (g)	0.1 N.KSCN ml.	Purity %	Wt. of Silver (g)		Current Efficiency
				Theor.	Expt.	
0.1	1.0250	8.40	90.62	1.3416	0.9288	69.23
0.3	1.2922	8.47	91.37	1.3416	1.1807	88.01
0.5	1.3263	8.60	92.78	1.3416	1.2305	91.72
0.7	1.2937	8.60	92.78	1.3414	1.2003	89.48
0.9	1.3119	8.30	89.54	1.3412	1.1747	87.58

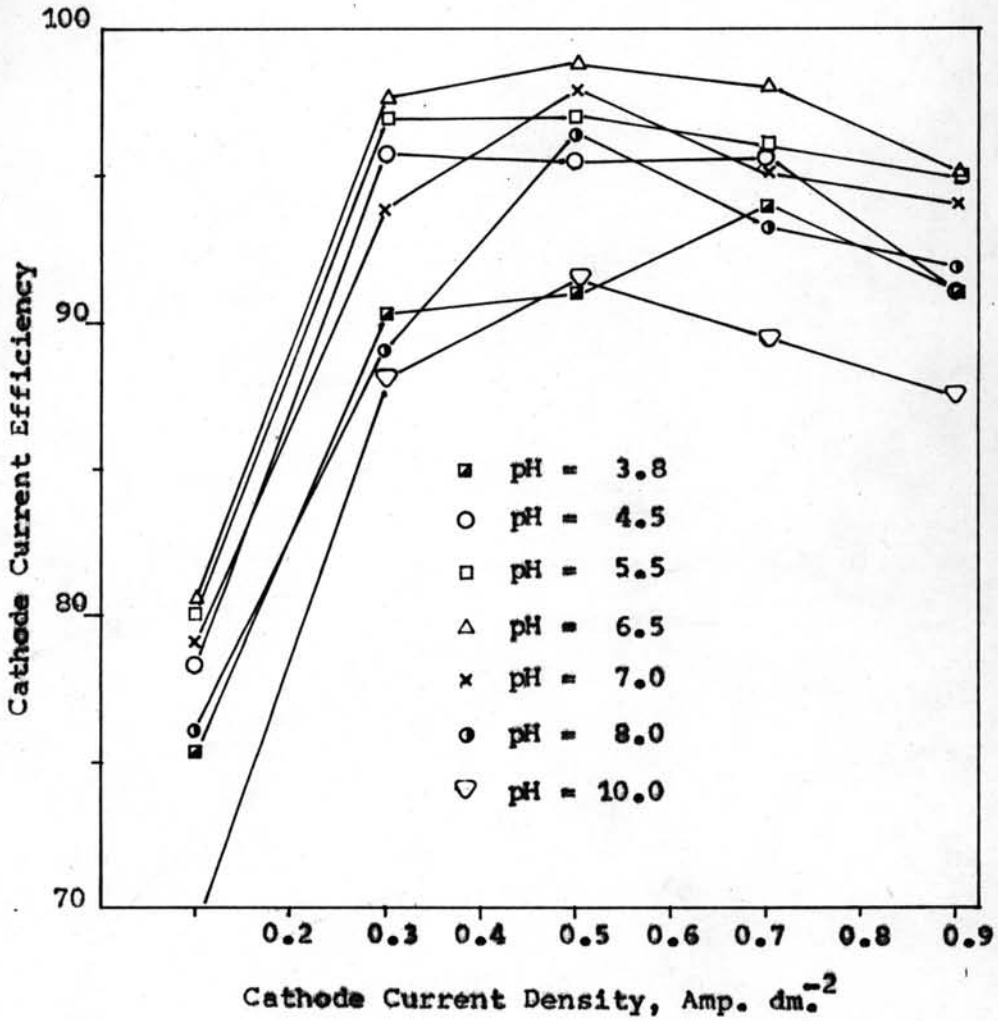

Figure 4.5 Effect of pH on cathode current efficiency., rotating speed = 800 r.p.m., temperature 30°c, E_{app} = 1.2 - 1.5 volts.

Table 4.15 Quantity of acid and base used to control pH of 500 ml. used fixing solution having original pH = 5.5

pH	12 N. NaOH ml.	Glacial HOAc ml.	Total addition ml.	% Volume Increase
3.8	1.12	17.72	18.84	3.76
4.5	0.38	2.04	2.42	0.48
5.5	1.15	-	1.15	0.23
6.5	3.23	-	3.23	0.64
7.0	3.97	-	3.97	0.79
8.0	4.53	-	4.53	0.90
10.0	4.81	-	4.81	0.96

4.5 Minimum Silver Concentration at Various Current Density.

The result of the experiment on quantitative analysis of silver concentration at which black particles (silver sulfide) were formed at the cathode for various current density are presented in Table 4.16 and are also presented graphically in Figure 4.6

All experiment were operated at the following condition : E_{app} = 1.2 - 1.5 volts. rotating speed = 800 r.p.m., temperature = 30°c, initial silver concentration of used fixing solution = 7.5 g /l , and pH = 6.5

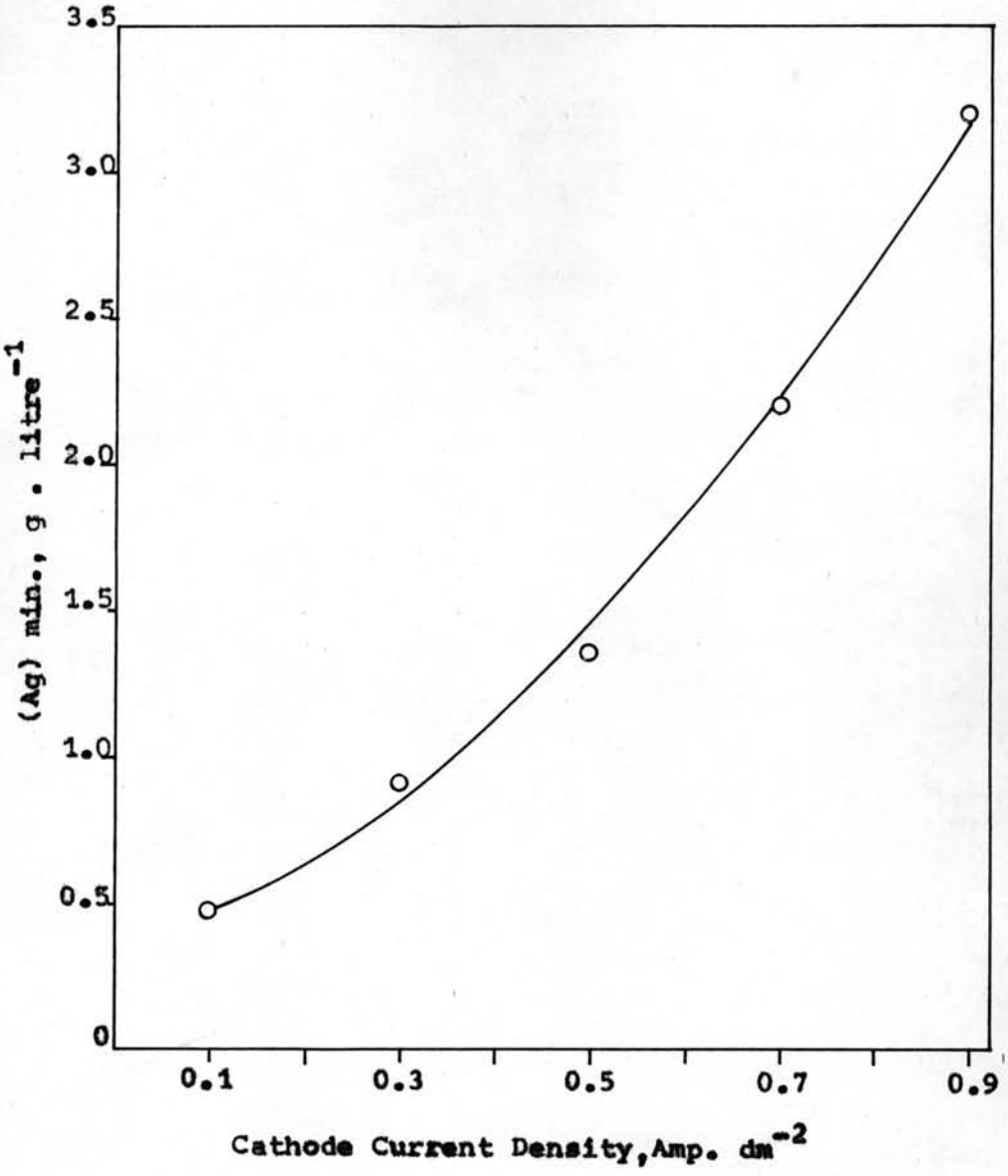

Figure 4.6 Dependence of silver concentration at which Silver sulfide occurred on cathode current density, rotating speed = 800 r.p.m., pH = 6.5, temperature = 30°c E_{app} = 1.2 - 1.5 volts.

Table 4.16 Experimental results of minimum silver concentration at which silver sulfide appeared, at various current density.

Current Density asd.	Dilution Ratio	Average Absorbance	Ag min g/litre.
0.1	1 : 100	22.17	0.47
0.3	1 : 100	42.50	0.91
0.5	1 : 1,000	6.33	1.35
0.7	1 : 1,000	10.33	2.20
0.9	1 : 1,000	14.83	3.20

4.6 Current Efficiency at Various Sodium Sulfite Concentration.

The results of the experiment on quantitative analysis of silver concentration at various time intervals for various sodium sulfite concentration are presented in Table 4.17, and the results of calculation on current efficiency for various sodium sulfide concentration are presented in Table 4.18 and are presented graphically in Figure 4.7

All experiment were operated at the following condition : E_{app} = 1.3 volts, current density = 0.5 asd. temperature = 30°c initial silver concentration of pure silver complex ($NaAgS_2O_3$) solution = 7.5 g /l at pH = 6.5

Table 4.17 Experimental results of silver concentration analysis by A.A.S. for various sodium sulfite concentration.

Time (min)	without Na_2SO_3		5 g. Na_2SO_3/litre		15 g. Na_2SO_3/litre		30 g. Na_2SO_3/litre	
	Av. Absorbance	Ag g /l	Av. Absorbance	Ag g /l	Av. Absorbance	Ag g /l	Av. Absorbance	Ag g /l
0	35.00	7.50	35.17	7.50	35.0	7.50	35.0	7.50
20	28.66	6.19	28.83	6.22	29.0	6.24	28.83	6.22
40	22.83	4.92	23.00	4.95	22.83	4.92	22.83	4.92
60	17.00	3.65	17.00	3.65	17.17	3.67	16.66	3.60
80	11.33	2.43	11.17	2.41	11.00	2.36	11.00	2.36
100	6.00	1.28	5.66	1.22	5.17	1.09	5.17	1.09

Table 4.18 Experimental results of current efficiency for various sodium sulfite concentration.

		Without Na_2SO_3		5 g. Na_2SO_3/l		15 g. Na_2SO_3/l		30 g. Na_2SO_3/l	
Time (min)	Wt. of Ag. Theor./ 20 min	Wt. of Ag. Expt./ 20 min	Current Efficiency	Wt.of Ag Expt./ 20 min	Current Efficiency	Wt. of Ag Expt./ 20 min	Current Efficiency	Wt. of Ag Expt./ 20 min	Current Efficiency
0	-	-	-	-	-	-	-	-	-
20	0.6708	0.655	97.64	0.640	95.40	0.630	93.91	0.640	95.40
40	0.6708	0.635	94.66	0.635	94.66	0.660	98.38	0.650	96.89
60	0.6708	0.635	94.66	0.650	96.89	0.625	93.17	0.660	98.38
80	0.6708	0.610	90.93	0.620	92.43	0.665	97.64	0.620	92.42
100	0.6708	0.575	85.71	0.595	88.70	0.635	94.66	0.635	94.66

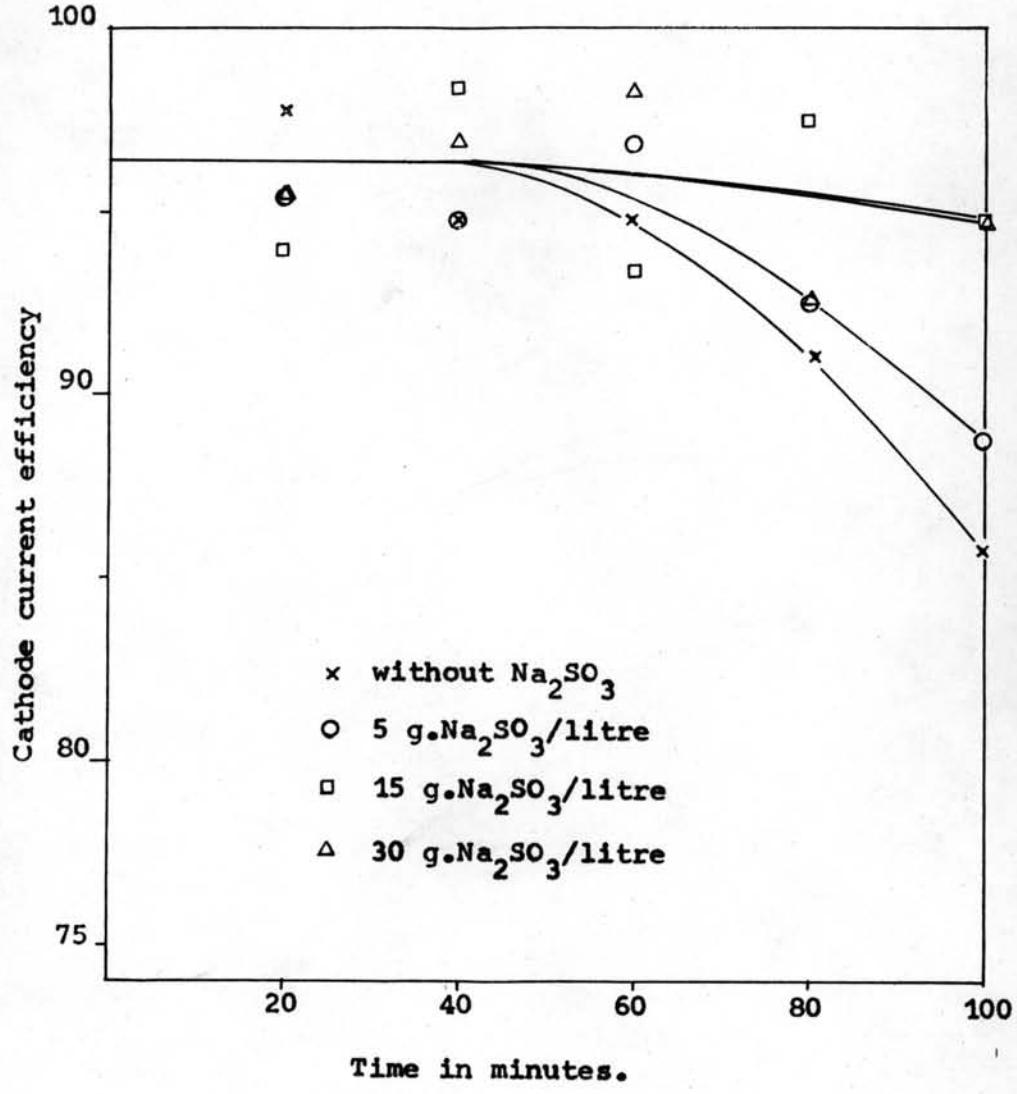

Figure 4.7 Effect of Sodium sulphite on current efficiency, rotating speed = 800 r.p.m., pH = 6.5, current density = 0.5 asd., Temperature = 30°c, E_{app} = 1.3 volts.

4.7 Current Efficiency of Various Fixing Solution at Optimum Condition.

The results, of the experiment on current efficiency determination of various fixing solution at optimum condition which have the following operating condition : E_{app} = 1.3, current density = 0.5 asd., rotating speed = 800 r.p.m., pH = 6.5, and temperature = 30°c, are presented in Table 4.19

All of these fixing solution were diluted to the same silver concentration, 5 g /l , with deionized water.

Table 4.19 Experimental results of current efficiency determination on different Type of fixing solution in comparism with pure silver complex + 15 g. Na_2SO_3 /litre.

Type of fixing solution	Wt. of Yield (g)	0.1 N.KSCN ml.	Purity %	Wt. of Ag Expt. (g)	Current Efficiency
B & W aerial film fixing solution	2.0183	9.10	98.17	1.9814	98.46
Color aerial film fixing solution	1.9687	9.20	99.25	1.9540	97.10
B & W negative film fixing solution	1.9951	9.05	98.63	1.9678	97.79
Color negative film fixing solution	1.9754	9.13	98.49	1.9456	97.68
X-ray film fixing solution	1.9832	9.17	98.92	1.9618	97.49

Table 4.19 Experimental results of current efficiency determination on different Type of fixing solution in comparism with pure silver complex + 15 g. Na_2SO_3 /litre. (continue)

Type of fixing solution	Wt. of Yield (g)	0.1 N.KSCN ml.	Purity %	Wt. of Ag Expt. (g)	Current Efficiency
Motion picture fixing solution	2.0109	8.90	96.01	1.9307	96.94
Pure silver complex + 15 g. Na_2SO_3 /litre.	1.9712	9.25	99.78	1.9669	97.74

Note. The operating time = 1 hr.,theoritical weight of recovery silver is equal to 3600 sec x 0.5 amp. x .001118 = 2.0124 g.